

Depassivation Behavior of Titanium Alloys in Strong Alkaline Aqueous Solutions

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INTRODUCTION

Concrete structures will be utilized at structural parts of facilities for geological disposal programs of nuclear waste. An overpack material will be exposed to strong alkaline ground water infiltrated through the concrete structures. Titanium alloys has been investigated as one of the overpack materials, because of it's high corrosion resistance in natural water and seawater environments. However, the potential-pH diagram¹⁾ for the system titanium-water shows that titanium could be dissolved in strong alkaline solutions with pH > 12.5 even at room temperature. Furthermore, it is apprehended that the active region is much expanded to an acidic region at higher temperatures. Therefore, quantitative data on depassivation pH, pH_d , for titanium alloys at various temperatures would be quite important in understanding corrosion behavior of titanium alloys in waste disposal conditions. Thus, the present study examined effects of solution temperature and composition on the pH_d of some titanium alloys.

EXPERIMENTAL

Two titanium alloys were used for two types of electrochemical measurements, namely, Ti-Gr.1 and Ti-Gr.-17. Two types of test solutions are employed in the present study: one is a synthetic seawater-originated ground water infiltrated through underground concrete structures and to be in equilibrium with concrete, and the other is NaOH solution. The former is, thus, solutions saturated with $\text{Ca}(\text{OH})_2$ and CaCO_3 with the addition of 0.55 mol /l of NaCl, and to be referred in the present study as a synthetic concrete equilibrium solution.

The measurement of free corrosion potential was conducted in aerated test solutions. The measurement of polarization curves were conducted in deaerated test solutions with the sweeping rate of 20 mV/min. The tests were conducted at three test temperature levels, namely, 25 , 55 and 80 .

RESULTS AND DISCUSSION

The steady-state corrosion potential, E_{SP} , of passive alloys like stainless steel and titanium alloys immersed in aqueous solutions is believed to change with respect to the pH of the solutions according to the following equation²⁾ without any temperature dependence, namely,

$$E_{\text{SP}} = 0.733 - 0.0591\text{pH} \quad (\text{V vs. SHE}) \quad (1)$$

When a specimen of Ti-Gr.1 was immersed and depassivated in a strong alkaline NaOH solution at 25 , changing the pH of the test solution to the acidic side gradually, the potential was ennobled abruptly at about 13.7 of pH and approached the linear relationship of the equation (1). This result showed that the specimen was passivated. A measurement was conducted to confirm this behavior by immersing a specimen for a long period

in the aerated NaOH solution of pH=13 at 25 . The free corrosion potential was found to be stable around the potential given by the equation (1).

On the other hand, the anodic polarization curves of the Ti-Gr.1 in the deaerated NaOH solutions of the pH of 12, 13, and 14 at 25 are shown in Fig. 1 as the solid lines. A dotted line in the figure is the cathodic polarization curve obtained in the aerated NaOH solution at pH=12. The free corrosion potential is given as an intersection of an anodic polarization curve and a cathodic polarization curve. Here, the anodic polarization curves for the pH of 12 and 13 cross the cathodic polarization curve in the passive region. However, the anodic polarization curve obtained at pH=14 behaves differently from those for lower pH, as exhibiting a large peak approximately at -0.9 V, and crossing the cathodic polarization curve in the less-noble region than -1 V. Thus, the pH_d for the system is found to be between 13 and 14, suggesting a fairly good agreement with the result obtained in the measurement of the free corrosion potential. Thus, we have concluded the pH_d of the Ti-Gr.1 in the solution is 13.7. Measurements with Ti-Gr.17 were conducted, and the results showed that the pH_d obtained were identical to those for the Ti-Gr.1. Thus, the pH_d were determined at three test temperatures, and two fitting equations were obtained from the results as follows;

for NaOH solution environments,
$$pH_d = -2.38 + 4790 (1/T) \quad (2)$$

and

for synthetic concrete equilibrium solution environments,
$$pH_d = -5.01 + 5538 (1/T) \quad (3)$$

(T : temperature, K)

REFERENCES

- 1) M. Pourbaix; "Atlas of Electrochemical Equilibria in Aqueous Solutions", NACE, Houston, Texas, USA (1974).
- 2) T. Fukuda and M. Akashi; Proc. Nuclear Waste Packaging-FOCUS'91, ANS, p.201 (1991)

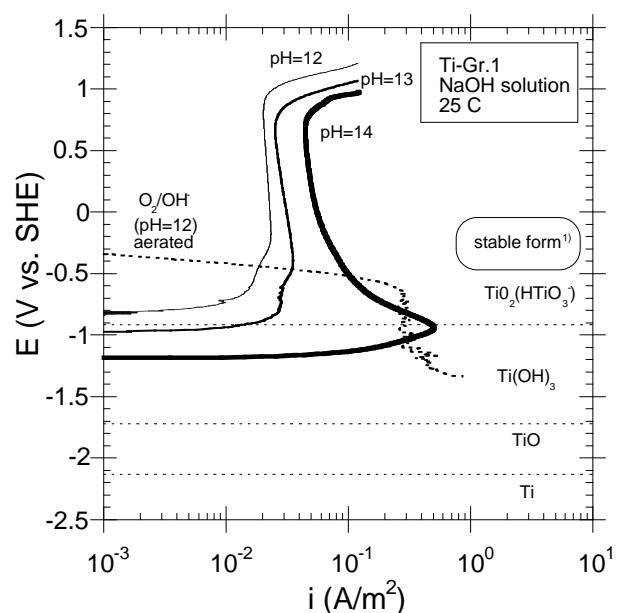


Fig. 1 pH dependence of the anodic polarization curves of the Ti-Gr.1 specimens in the NaOH solution at 25 .